



A model compound (methyl oleate, oleic acid, triolein) study of triglycerides hydrodeoxygenation over alumina-supported NiMo sulfide

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ABSTRACT

We studied hydrodeoxygenation of model compounds for vegetable oil into diesel-range hydrocarbons on a sulfided NiMo/γ-Al₂O₃ catalyst under trickle-flow conditions. Methyl oleate (methyl ester of oleic acid, a C18 fatty acid with one unsaturated bond in the chain) represented the C18 alkyl esters in natural fats, oils and greases. The effect of temperature and pressure on activity and product distribution (mainly C17 and C18 hydrocarbons) were studied. Hydrolysis of the methyl ester results in fatty acid intermediates, which are converted by direct hydrodeoxygenation to C18 hydrocarbons or decarbonated (by decarbonylation or decarboxylation) to C17 hydrocarbons. Reactant inhibition is more pronounced for the former route. The reaction is hardly inhibited by H₂S, H₂O, CO and tetralin solvent. H₂S and to a lesser extent H₂O increase the C17/C18 hydrocarbon ratio, because they inhibit direct hydrodeoxygenation more than decarbonation. The catalyst surface contains different sites for direct hydrodeoxygenation and decarbonation reactions. During methyl oleate HDO, the catalyst slowly deactivated, mainly due to blocking of Lewis acid sites of the alumina support that catalyze methyl oleate hydrolysis. The catalyst was much more active in the HDO of triolein (glyceryl trioleate, representative triglyceride model compound) than in methyl oleate HDO, to be attributed to very facile hydrolysis of triglycerides. Although the overall kinetics of methyl oleate and triolein HDO were similar, our results show that the catalyst and H₂S play a much more important role in the hydrolysis of methyl oleate than in hydrolysis of triglycerides.

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1. Introduction

Environmental concerns about global warming and the foreseen dwindling of fossil reserves are the main drivers for the search of alternative renewable energy resources. Although other forms of renewable energy are becoming increasingly important to cover energy demand, it is expected that liquid hydrocarbons will remain important as transportation fuels in the coming decades. These transportation fuels are mainly obtained from crude oil feedstock [1]. Environmental legislation mandates the use of biofuels derived from renewable biomass resources [2]. Demand is currently mostly covered by first-generation biofuels, which are manufactured from edible biomass such as starch-rich or oily plants. Sugars from sugar- and starch-rich crops can be fermented into bio-ethanol. Biofuels generated from lignocellulosic (second-generation) biomass do not compete with food production or land use. Both biochemical and thermochemical processes can be used to convert lignocellu-

losic biomass into biofuels. The latter include technologies such as pyrolysis, gasification, supercritical fluid extraction, and direct liquefaction [3,4].

Vegetable oils and animal fats are triglycerides that can be converted to transportation fuels. Two important routes have been developed to convert triglycerides into diesel-range transportation fuels. Biodiesel is comprised of fatty acid methyl esters (FAMEs) obtained by base- or acid-catalyzed transesterification of vegetable oils with an alcohol. These reactions do not involve deoxygenation of the feedstock. FAMEs are unstable on storage and may also cause problems when used in combustion engines, which limits the amount of biodiesel that can be blended in diesel fuel [1,2]. An alternative approach involves the direct hydrodeoxygenation (HDO) of triglycerides into hydrocarbons. Usually, diesel resulting from HDO is called “green diesel” or “renewable diesel” to distinguish it from “biodiesel”. Compared with biodiesel, green diesel is compatible with existing engines and has better fuel properties because of its higher cetane number, higher energy density and very low sulfur content [1,5]. It is also possible to obtain lighter hydrocarbons for the jet fuel or gasoline pool by using catalysts with strong acid sites.

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Upgrading of this feedstock can either be done by hydroprocessing of the triglycerides only or by co-feeding them in petroleum-refining processes. The latter has been explored to some extent [6,7], while the former appears to be the preferred option in currently technology for upgrading of triglycerides. For instance, the UOP/ENI Ecofining processes involves hydrotreating followed by isomerization [8]. Neste operates plants in Finland, The Netherlands and Singapore that convert palm oil and waste animal fat into green diesel by hydrotreating [9]. The resulting fuels are not a substitute of fossil fuels, but they are blended with fossil fuels to boost their properties. The catalyst determines to a large extent the yield and product distribution during triglycerides conversion. Many types of catalysts have been explored for direct hydrotreating of triglycerides, and they are usually comprised of zeolites or conventional hydrotreating catalysts used in petroleum refining. Aside from the hydrogenation functions of metal sulfides or noble metals, the oxidic support can facilitate hydrocracking, which is important when a boiling point shift to gasoline-range hydrocarbons is required [6,10]. Hydroprocessing of triglycerides with sulfided NiMo catalysts yields green diesel [11,12]. A comparative study of Sotelo-Boyás et al. demonstrated the preference of NiMo/γ-Al₂O₃ over Pt/zeolite systems for obtaining diesel-range hydrocarbons [13]. Alumina-supported NiMoS (and CoMoS) catalysts have already been extensively studied in the context of hydrotreating of petroleum fractions. Several excellent reviews are available [14–18].

Despite the above-mentioned contributions on hydrotreating real triglyceride feedstock [11,12], there are relatively few works that deal with pertinent aspects of supported NiMoS catalysts such as the reaction mechanism and catalyst stability [1,5,6,19–28]. A concern with respect to deactivation is that oxygen from the feedstock can oxidize the active metal sulfide phase [21,29]. Usually, when studying catalysts for the HDO of triglycerides, model compounds are used such as oleic acid [30,31] and methyl oleate [32,33]. These previous works did not focus on establishing a clear reaction network nor did they investigate the long-term stability of the catalyst. Detailed investigation of these aspects has been carried out by the group of Krause, who employed methyl heptanoate as a gas phase-model compound to study the kinetics and mechanism of HDO reactions of triglycerides [22–25,34,35].

In the present work, we employ more realistic model compounds for the triglycerides present in vegetable oil feedstock to study the behavior of sulfided NiMo/γ-Al₂O₃ under trickle-flow conditions. Methyl oleate, which is the methyl ester of the C18 fatty acid containing one double bond, was used because of the high abundance of C18 alkyl esters in natural fats, oils and greases. Usually, 50–90% of such feedstock has a carbon length of 18 of which 50–95% is comprised of unsaturated C18 chains [36]. Oleic acid was included to investigate the reactivity of intermediate acids. During investigation of the kinetics of methyl oleate and oleic acid HDO, it was observed that the NiMoS/Al₂O₃ catalyst slowly deactivated. Therefore, spent catalysts were extensively characterized, amongst others by XPS and TEM, in an attempt to understand this deactivation. Finally, the activity and selectivity of triolein (glyceryl trioleate), which is a representative triglyceride model compound for vegetable oil feedstock, were compared with the performance of the catalyst in methyl oleate HDO.

2. Experimental methods

2.1. Materials

A commercial NiMo/Al₂O₃ catalyst (Shell, extrudates) was grinded and sieved to obtain particles with sizes between 125 µm and 250 µm. This catalyst was used for the activity tests of the

hydrodeoxygenation of methyl oleate and oleic acid. A home-made NiMo/Al₂O₃ catalyst was employed to investigate catalyst deactivation. This catalyst was prepared by incipient wetness impregnation of γ-alumina (Ketjen CK-300, pore volume 0.66 ml/g, surface area 263 m²/g), with an aqueous solution of Ni(NO₃)₂·6H₂O (Sigma-Aldrich) and ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄ (Merck). Before impregnation, the support was dried overnight at 110 °C. After applying the solution, the sample was dried at ambient temperature for 1 h and overnight at 110 °C. Afterwards, the catalyst was calcined at 450 °C for 2 h in flowing air (ramp rate 10 °C/min). The Mo loading of the calcined catalyst was 8.3 wt% and the Ni/Mo atomic ratio was 0.3, as determined by ICP-OES elemental analysis (Spectro CIROS CCD spectrometer, samples dissolved in 1/1/1 vol mixture of HF/HNO₃/H₂O).

Methyl oleate (ABCR, 92%), oleic acid (VWR, 96%) and triolein (ABCR, 80%) were used as received. Analysis of the methyl oleate feedstock by gas chromatography showed the presence of three main isomers of octadecenoic methyl ester, making up 86 wt% of the feedstock. The feedstock also contained about 4 wt% C18 methyl esters with two unsaturated C–C bonds (methyl linoleate) and three unsaturated C–C bonds (methyl linoleate). In total, six isomers of these compounds were detected. The remainder of the methyl oleate feed was 10 wt% of methyl palmitate, which is a C16 methyl ester. Elemental analysis showed the presence of a very small amount of chlorine (3 ± 3 mg/kg). The oleic acid feedstock contained 70 wt% of two isomers of octadecenoic acid. The content of C18 carboxylic acids with two unsaturated C–C bonds (linoleic acids) was about 15 wt%. Octadecanoic acid (stearic acid) was present in an amount of 4 wt%. The hexadecanoic acid (palmitic acid) content was about 8 wt%. Triolein is the ester of glycerol and three unsaturated fatty acid molecules. These fatty acids can be either *cis* or *trans* as well have different positions of the double bond. The triolein feedstock is comprised of several isomers; the exact composition was not determined.

2.2. Catalytic activity measurements

Catalytic HDO activity experiments were carried out in a fixed-bed Hastelloy reactor, which was heated in a three-zone oven. Thermal mass flow controllers were used for the supply of H₂, H₂S and CO gases. The liquid feed was supplied by a Shimadzu LC-20AD pump. All tubing was heated after the point of introduction of the liquid feed into the gas stream to avoid condensation of reactants and products. The catalyst bed consisted of 0.1 g catalyst mixed with 2.5 g SiC. Before the catalyst bed, a pre-bed was placed consisting of 5 g SiC in order to establish trickle-flow conditions [37]. Prior to loading the reactor, the catalyst was calcined in static air in an oven at 400 °C for 1 h in order to avoid deviations in sulfidation due to different hydration levels. The catalyst was sulfided at 15 bar in a 60 ml/min flow of 10 vol% H₂S in H₂. During sulfidation, the temperature was increased at a rate of 6 °C/min to 400 °C followed by an isothermal period of 2 h [38]. Then, the temperature of the catalyst bed was lowered to 260 °C and the total pressure was increased to 60 bar. The packed bed was then wetted by maintaining a liquid flow rate of 1 ml/min for 15 min. The reaction was started by adding the gases to the feed. The feed consisted of a mixture of 20 wt% of either methyl oleate, oleic acid, or triolein in 1,2,3,4-tetrahydronaphthalene (tetralin, ≥98%, Merck). The weight hourly space velocity (WHSV) during methyl oleate HDO measurements was 6.5 h⁻¹. The gas-to-oil ratio (GOR) was 10,320 Nl kg⁻¹ h⁻¹. The gas phase typically consisted of H₂ and 2000 ppm H₂S (range 500–10,000 ppm). In activity tests, the influence of H₂S, CO and H₂O on the reaction rate was investigated. CO was co-fed as a pure gas (99.995%, Linde) using a thermal mass flow controller (range 0–45,000 ppm). Water was generated in-situ by co-feeding isopropanol (99.5%, Aldrich), which is rapidly

converted to water and propane under the given reaction conditions. The range up to 3500 ppm was chosen such as to represent the amount of water formed at a methyl oleate conversion of 50%. Only at the highest isopropanol concentration, trace amounts of unconverted isopropanol were detected by GC analysis.

The liquid phase of the reactor effluent was analyzed on an Rx-5Sil MS column ($L = 30\text{ m}$, $d_i = 0.32\text{ mm}$, $d_f = 1.2\text{ }\mu\text{m}$) placed in an Interscience FocusGC gas chromatograph equipped with a flame ionization detector (FID). Injection was done by a ROLSI system from a small reservoir placed directly after the reactor outlet. In initial experiments, the gas phase was analyzed using an online gas chromatograph (Interscience CompactGC, RTx-1 equipped with FID, RT-U-Bond and a RT-Mol Sieve 5 Å, both employing TCD). The composition of the gas phase was determined after condensation of the reactor effluent stream in a condenser kept at 50 °C. Additional offline analysis of liquid effluent samples was done by GC-MS (Shimadzu QP5050, Rx-5MS: $L = 30\text{ m}$, $d_i = 0.25\text{ mm}$, $d_f = 0.25\text{ }\mu\text{m}$; RTx-1707: $L = 60\text{ m}$, $d_i = 0.25\text{ mm}$, $d_f = 0.25\text{ }\mu\text{m}$ and Stabilwax-DA column: $L = 30\text{ m}$, $d_i = 0.32\text{ mm}$, $d_f = 0.50\text{ }\mu\text{m}$). By combining gas and liquid phase analysis it was established that the mass balance was $96\% \pm 4\%$. HDO conversion is defined as the product yield of C17 and C18 hydrocarbons, that is the fraction of the feedstock (including interconverted oxygenates) from which oxygen was completely removed:

$$X_{\text{HDO}} = \frac{n_{\text{C17}} + n_{\text{C18}}}{n_{\text{C17}} + n_{\text{C18}} + n_{\text{oxy}}} \times 100\% \quad (1)$$

n_{C17} , n_{C18} and n_{oxy} represent the amount of C17, C18 and oxygenated molecules in the product mixture. Reaction orders were determined using power rate law expressions, while the apparent activation energy was determined from an Arrhenius plot. We also considered the distribution of oxygen containing compounds in the product stream. In this analysis we included the unconverted feedstock. We further distinguished the C17 and C18 selectivity in which olefins and paraffins were lumped:

$$S_{\text{C17}} = \frac{n_{\text{C17}}}{n_{\text{C17}} + n_{\text{C18}}} \times 100\% \quad (2)$$

Yield was computed by multiplying conversion with corresponding selectivity. We also determined the fraction of olefins for each of the two C17 and C18 fractions.

2.3. Catalyst characterization

Catalyst deactivation was studied by carrying out the HDO reaction without a pre-bed and diluent to obtain the spent catalyst in a form amenable for further surface analysis. We verified that the home-made NiMo/Al₂O₃ showed similar performance as the commercial catalyst used in the kinetic study (Supplementary information, Fig. S1). Reactions were performed at 260 °C, 50 bar, a GOR of 4750 Nl kg⁻¹ h⁻¹ and a WHSV of 6.5 h⁻¹. The feed also contained 2000 ppm H₂S. The HDO reaction run was ended by stopping the liquid feed flow, followed by cooling the reactor in the feed gas to room temperature. At room temperature, the catalyst was rinsed with n-heptane, flushed with He and then removed and stored in a nitrogen-flushed glove box before further characterization.

For X-ray photon spectroscopy (XPS) analysis, a transfer holder was used to transfer the well-crushed sample from the nitrogen-filled glove box to the XPS apparatus (no air exposure). The XPS measurements were carried out on a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source and a delay-line detector (DLD). Spectra were obtained using the aluminium anode (Al K α = 1486.6 eV) operating at 150 W. Survey scans were measured at a constant pass energy of 160 eV and region scans at 40 eV. The background pressure was 2×10^{-9} mbar. Energy correction was performed by using the C 1 s peak of adventitious carbon

at 284.5 eV as a reference. The resulting spectra were fitted using CasaXPS.

Accurate determination of the dispersion and stacking degree requires that the spent catalysts is removed from the reactor to the electron microscopy without exposure to air [39]. For analysis by transition electron microscopy (TEM), glass ampules were used to transfer the catalysts to the TEM laboratory at Delft University of Technology. The ampules were then loaded in an argon-filled glove box and opened. The sample was crushed in *n*-hexane using a mortar so as to obtain a suspension, which was then dropped on a Cu holey carbon TEM grid (Quantifoil). The solvent was slowly evaporated at room temperature, after which the TEM grid was placed in a specially designed vacuum transfer TEM holder. With this, the TEM grid can be transported to the TEM without any contact to air. TEM measurements were carried out using an FEI Tecnai F20ST/STEM, operated at an accelerating voltage of 200 keV. Images were obtained using a Gatan Ultrascan CCD camera (4k × 4k) in bright-field mode, at a magnification of 440 k. Per sample, about 50 micrographs were taken. Detailed analysis of these micrographs was carried out by measuring the length and stacking degree using the ImageJ software. In this way, between 600 and 1100 particles were analysed per sample.

²⁷Al Nuclear Magnetic Resonance (NMR) measurements were performed on an 11.2 T Bruker DMX500 NMR spectrometer operating at 130 MHz. An amount of ~10 mg of well-hydrated sample was packed in a 2.5-mm zirconia rotor. The ²⁷Al MAS NMR measurements were done using a Bruker 2.5-mm MAS probehead spinning at 20 kHz. Spectra were recorded with a single pulse sequence with an 18° pulse duration of 1 μs and an interscan delay of 1 s. A saturated Al(NO₃)₃ solution was used for ²⁷Al NMR shift calibration.

X-ray diffraction (XRD) patterns were recorded on a Bruker D4 Endeavor powder diffraction system using Cu K α radiation with a step size of 0.03° s⁻¹ in the 2 Θ range 10–90°.

Thermal gravity analysis (TGA) was performed using a Mettles Toledo TGA/DSC 1 instrument. Weight-loss curves of spent catalysts were recorded while heating to 800 °C in uncovered alumina crucibles at a rate of 5 °C/min in an air flow at 20 ml/min.

N₂ physisorption was performed on a Micromeritics Tristar 3000. Samples (~25 mg) were outgassed at 400 °C for 3 h prior to sorption measurements. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (S_{BET}) from the adsorption data obtained ($p/p_0 = 0.05–0.25$). The mesopore volume (V_{meso}) and the mesopore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method on the adsorption and desorption branch of the isotherm.

Diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) was done using a Bruker Vertex 70 v FTIR spectrometer. Samples were loaded in a micro sample cup and measured at room temperature in the Praying Mantis accessory (Harrick Instruments) flushed with dry nitrogen. KBr (Sigma Aldrich, spectroscopy grade) was used as the reference sample. Spectra were recorded with a liquid nitrogen cooled MCT detector in the range 400–3950 cm⁻¹ at 4 cm⁻¹ resolution by averaging 100 individual scans.

UV Raman spectra were recorded with a Jobin–Yvon T64000 triple stage spectrograph with a spectral resolution of 2 cm⁻¹. The 325 nm line of a Lexel 95-SHG laser was used as the excitation source. The power of the laser on the sample was 2 mW.

3. Results and discussion

This paper is organized in the following manner. We mention the main aspects of the HDO reaction network of fatty methyl esters based on literature before discussing results for HDO of methyl oleate and oleic acid. We then investigate catalyst stability during methyl oleate HDO by characterizing spent samples. Finally, the

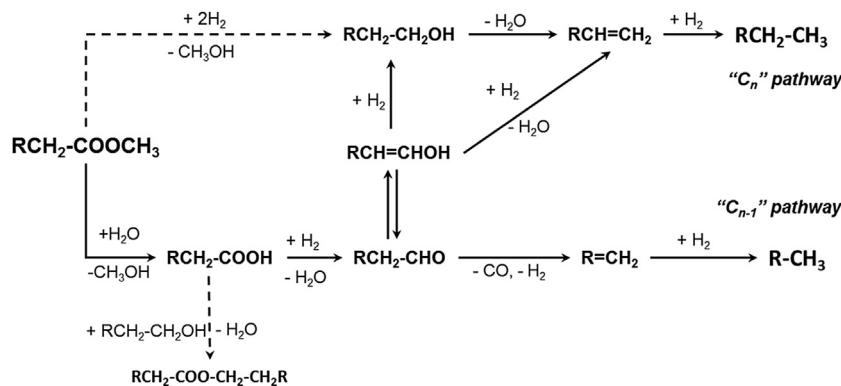


Fig. 1. Proposed mechanism of hydrodeoxygénéation of methyl oleate involving hydrolysis to oleic acid followed by deoxygenation to the aldehyde. Decarbonylation of the aldehyde results in C17 hydrocarbons (olefins and paraffins). C18 hydrocarbons are obtained by direct hydrogenation or hydrogenation of a keto intermediate in combination with dehydration. Direct hydrogenation of the methyl esters is indicated from completeness (dashed line).

performance of sulfided NiMo/ γ -Al₂O₃ in glyceryl trioleate HDO is evaluated and a comparison is made between the different model compounds.

Fig. 1 shows the reaction network for the hydrodeoxygénéation of methyl esters [6,20,22,26]. Methyl esters can either be hydrolyzed to the fatty acid or hydrogenated to the fatty alcohol. Direct hydrogenation of esters to the corresponding alcohols is very difficult and requires high pressure and temperature and specific catalysts [40]. Accordingly, this pathway is not expected to contribute significantly to the overall conversion rate on sulfide catalysts, which is in keeping with the conclusion of Şenol et al. in their study of the HDO of methyl heptanoate using a similar metal sulfide catalyst [25]. Hydrolysis of esters, on the other hand, is more facile, which is usually considered to involve water. Şenol et al. emphasized the role of Lewis acid sites of the alumina support as catalysts for ester hydrolysis [22]. In follow-up work by the same group [35], an additional pathway was suggested to involve nucleophilic SH groups, as was evident from the presence of small amounts of thiols. Although we did not observe such sulfur-containing compounds in the present study, likely because the residence time of the octadecanoate esters was longer in our trickle-flow operated reactor than of the heptanoate esters in the gas-phase study by Krause and co-workers [24], we also observed increased contribution of decarbonylation (N.B.: decarbonylation refers to either decarboxylation or decarbonylation) reactions with increasing H₂S content of the feed. Methyl esters are typically less prone to hydrolysis than compounds containing β -hydrogen atoms such as triglycerides [41]. Murzin and co-workers argued that hydrolysis of the starting fatty alkyl ester to the fatty acid and the accompanying short-chain alcohol only occurs for methyl esters [42]. This was, however, contradicted in work by the group of Krause [23,35], in which comparison of methyl and ethyl esters showed similar product distributions. The fatty acid product from reactant hydrolysis can convert via an aldehyde intermediate to a shorter hydrocarbon by removal of CO or to the corresponding alcohol by hydrogenation. A side-reaction involves the reaction of the fatty acid with fatty alcohol intermediates to heavy esters. The formation of both C17 and C18 hydrocarbons during the HDO of oleic acid strongly suggests that fatty acids are the dominant reaction intermediate in the formation of these products during methyl oleate HDO [26]. C18 hydrocarbons are formed by hydrogenation of these intermediate fatty acids to aldehydes and alcohols, which then undergo hydrodeoxygénéation to yield C18 hydrocarbons. We use the term “direct hydrodeoxygénéation” or “direct HDO” for this route, where all the oxygen is removed as water. We use the term “hydrodeoxygénéation” or “HDO” for the overall conversion of oxygenated reactant molecules to C17 and C18 molecules free from oxygen. C17 hydrocarbons

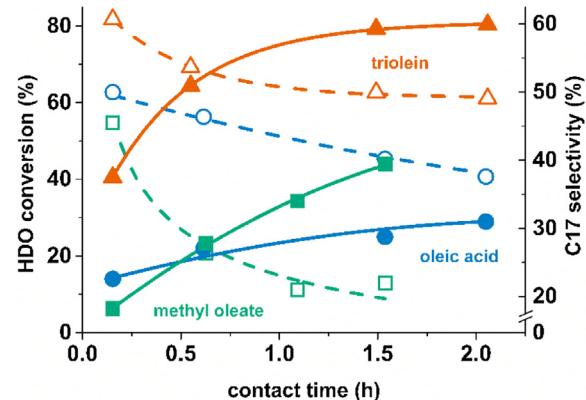


Fig. 2. HDO conversion (left, closed symbols) and C17 selectivity (right, open symbols) with respect to contact time of methyl oleate (■), oleic acid (●), or triolein (▲). The lines are meant to guide the eyes. Reaction conditions: $T = 260^\circ\text{C}$, $p = 60$ bar, GOR = $10,320 \text{ NL kg}^{-1} \text{ h}^{-1}$ with $2000 \text{ ppm H}_2\text{S}$ in the feed.

derive from decarbonylation (CO removal) or decarboxylation (CO₂ removal) [22,23]. Using online gas chromatography, we established that methane was the dominant reaction product in the gas phase. Only minor amounts of CO and CO₂ were observed in these experiments, while methanol was only seen in trace amounts. Methanol is much more reactive than the methyl esters. Under the given reactions conditions, CO and CO₂ are rapidly converted to methane and water via reverse water gas shift and methanation reactions [6,23]. Thermodynamic calculations show that nearly all CO and CO₂ can be converted to CH₄ at the high H₂/(CO+CO₂) ratio. Accordingly, most of the oxygen atoms from the feedstock will leave the reactor in the form of water. Because of this, we cannot distinguish between different pathways for C removal and we use the term “decarbonylation”. It is usually assumed that decarbonylation of the intermediate aldehydes is preferred over direct decarboxylation of the acid intermediate [22,43].

3.1. HDO of methyl oleate

The reaction temperature and reaction pressure were 260°C and 60 bar for the methyl oleate and oleic acid HDO measurements. The reactor feed consisted of 20 wt% methyl oleate dissolved in tetralin. The reaction orders with respect to methyl oleate were determined by varying the reactant concentration in the feed mixture. In these experiments, the total liquid flow rate was not changed with the purpose to maintain similar trickle-flow conditions. Fig. 2 shows overall HDO conversion and C17 selectivity of methyl oleate for

the sulfided NiMo/Al₂O₃ catalyst as a function of the contact time τ (τ is 1/WHSV in h).

The main HDO reaction products observed during methyl oleate HDO were octadecane, octadecenes, heptadecane and heptadecenes. No cracking was observed, which is expected when using the weakly acidic γ -alumina support [32,33]. In addition, the saturated C18 methyl ester (methyl stearate), octadecanoic (stearic) acid and octadecenoic (oleic) acid were observed among the reaction products. Fatty alcohols and fatty aldehydes were not detected by online GC analysis or by GC-MS analysis of the condensed reactor effluent. From the very small amounts of stearyl stearate (octadecyl octadecanoate), we infer that saturated fatty alcohols such as 1-octadecanol are intermediates of the overall reaction. Fatty alcohols will rapidly react with the intermediate fatty acids to heavy esters [26]. Similar types of products were observed from the conversion of the C16 methyl ester impurities present in the feedstock. Careful analysis showed that the reaction effluent did not include ethers [6,22] or thiols. Thiols have been reported earlier as the products from reaction of alkyl esters with H₂S and reactions of olefins with H₂S [22]. The reactivity of tetralin under the given reaction conditions was negligible.

The HDO reaction rate exhibited first-order behavior with respect to the reactant (integral reaction order 1.0 ± 0.02). Internal mass-transfer limitations were excluded on the basis of activity data obtained with different catalyst particle sizes [44]. External mass transfer limitations were excluded on the basis of the apparent activation energy (*vide infra*). With increasing HDO conversion, the C17 selectivity decreases substantially. This trend shows that the decarbonation route is affected in a different manner by HDO conversion than direct hydrodeoxygenation.

Fig. 3a reports the distribution of oxygenates as a function of the contact time. A significant fraction of methyl oleate was hydrogenated to methyl stearate. The methyl stearate selectivity was 70% at the shortest contact time and around 90% for longer contact times. This shows that hydrogenation of C=C double bonds in the methyl ester occurs at higher rate than hydrolysis and hydrogenation reactions of the ester functionality. The selectivity to oleic acid strongly decreased for longer contact times, confirming that oleic acid is a reaction intermediate. The rates of *cis-trans* isomerization of oleic acid and methyl oleate were high.

We then investigated the influence of H₂S, CO and H₂O on the performance. In all activity tests, H₂S was fed to the reactor in order to keep the active phase of the catalyst in the sulfided state [23,45]. Under reference conditions, the reactor feed contained 2000 ppm H₂S. Without H₂S, it was observed that the catalyst quickly lost its activity. Despite the presence of H₂S under reference conditions, the catalyst slowly deactivated over time. This aspect will be extensively investigated below. Fig. 4 shows the influence of the H₂S concentration on the HDO of methyl oleate. H₂S slightly inhibited the overall HDO conversion. The reaction order with respect to H₂S was around -0.09 ± 0.05 .

Fig. 4b shows that, with increasing H₂S concentration in the feed, the selectivity shifted from C18 to C17 hydrocarbons. The highest C17 yield was observed at a H₂S concentration of 8000 ppm (Fig. 4a). The group of Krause also reported that H₂S increased the rate of decarbonation in the HDO of methyl heptanoate on a NiMoS/ γ -Al₂O₃ catalyst [24]. These findings indicate that decarbonation is promoted by H₂S, while direct HDO is inhibited by H₂S. Consistent with the latter, it is also seen that the olefins yield increased slightly with H₂S concentration (Fig. 5b), demonstrating that H₂S inhibits hydrogenation. Fig. 6 shows the distribution of oxygenated products as a function of the H₂S concentration. H₂S also strongly inhibited the hydrogenation of methyl oleate to methyl stearate, and it led to a small increase of the amount of the oleic acid intermediate.

We then investigated the effect of CO and H₂O. In addition to competitive adsorption, water can also affect performance by oxidizing the active metal sulfide phase [23]. The results of these activity tests are shown in Fig. 7.

It is seen that CO hardly affected the HDO conversion and selectivity. This may in part be due to the rapid conversion of CO to methane, but also to the weak interaction of CO with the metal sulfide phase [46]. Water was in-situ generated by adding 2-propanol to the feed. It was verified that 2-propanol was completely converted to propane and water. At low H₂O concentrations (<5000 ppm), the HDO activity decreased slightly and then remained constant at higher water concentrations. The decrease of the HDO activity at these low concentrations led to slightly higher C18 selectivity. Water may play a role in the keto-enol isomerization step, which is relevant to the hydrogenation of the fatty aldehyde to the fatty alcohol (*vide infra*). This reaction competes with decarbonation that yields C17 hydrocarbons. In conclusion, the competitive adsorption of water only plays a minor role, in keeping with the finding that water hardly affected the HDO of methyl heptanoate over a NiMo sulfide catalyst [23]. Krause and co-workers argued that this is due to the compensating effect of H₂S for the inhibition of water.

We also investigated the effect of temperature on the HDO of methyl oleate. When the temperature was increased from 260 °C to 300 °C, the overall HDO conversion strongly increased (Fig. 8). The apparent activation energy was 193 kJ/mol, similar to experimental [47] and calculated values [27]. The strong temperature dependence indicates that internal and external mass transfer limitations are absent [44]. At higher temperature, slightly more C17 products were formed and more methyl stearate was formed. The observation that more oleic acid was observed at higher methyl oleate conversion implies that the further conversion of oleic acid is also a slow step in the overall mechanism. Significant differences were also observed in the olefins selectivity (Supplementary information, Fig. S2). At higher temperatures, less C18 olefins and more C17 olefins were obtained.

We also evaluated the influence of tetralin, which is used as the solvent for methyl oleate and to maintain trickle-flow operation. Fig. 7 shows the HDO conversion and selectivity as a function of the concentration of tetralin at constant WHSV. With increasing tetralin content the HDO conversion decreased. This could be due to competitive adsorption of tetralin on the active sites, but it is more likely related to the decrease of the liquid hold-up in the reactor with decreasing tetralin content at constant reactant WHSV. The decreased liquid hold-up favored direct HDO over decarbonation, which can be attributed to solubility differences of hydrogen in methyl oleate and tetralin. We also carried out one reaction with a pure methyl oleate feed in the absence of tetralin and observed similar products.

3.2. HDO of oleic acid

Fig. 2 shows the HDO conversion of oleic acid as a function of the contact time. Similar products were formed as observed during methyl oleate HDO, which confirms the role of oleic acid as a major reaction intermediate in the HDO of methyl oleate. Also in these experiments, we observed that all initial CO and CO₂ products were converted into methane, as recently also confirmed by isotopic labeling by Szarvas et al. [31]. The reaction rate for oleic acid HDO was substantially higher than for methyl oleate HDO and the reaction of oleic acid was first-order in the reactant. The oxygenates distribution is shown in Fig. 3b. Trends with respect to contact time are similar to those observed for methyl oleate HDO (Fig. 3a). During oleic acid HDO, much larger amounts of stearyl stearate were observed than during methyl oleate HDO. Stearyl stearate is the product of esterification of fatty acid intermediates

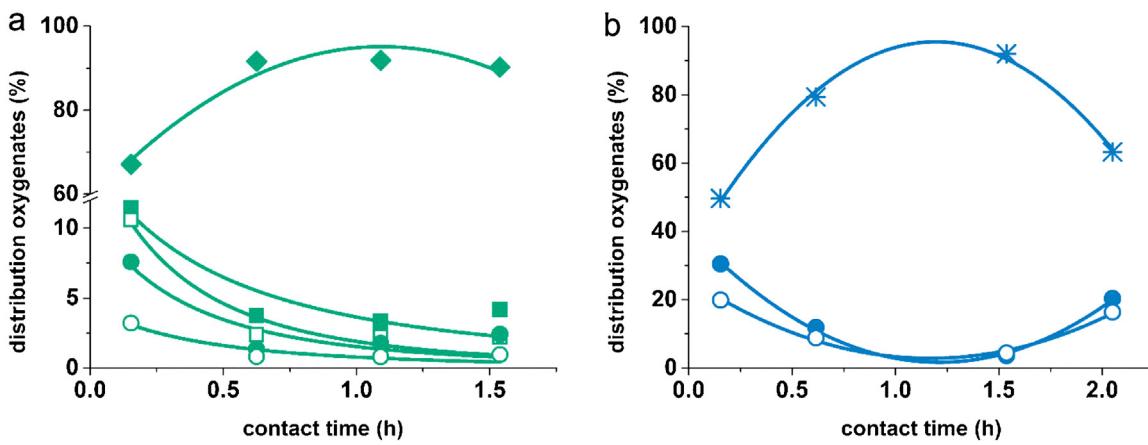


Fig. 3. Distribution of oxygenates in the effluent stream with respect to the contact time for (a) methyl oleate and (b) oleic acid reactants. Shown are methyl stearate (♦), methyl oleate (■), oleic acid (●), and stearic acid (*). Open and closed symbols represent *cis*- and *trans*-isomers respectively. Reaction conditions: $T=260^{\circ}\text{C}$, $p=60\text{ bar}$, $\text{GOR}=10,320\text{ Ni kg}^{-1}\text{ h}^{-1}$ with 2000 ppm H_2S in the feed.

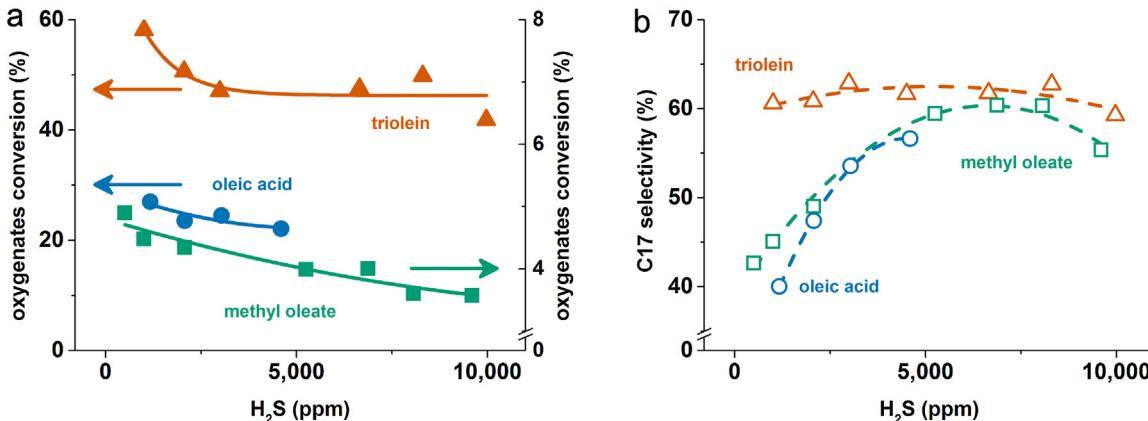


Fig. 4. HDO conversion (a) and C17 selectivity (b) with respect to concentration of co-fed H_2S from methyl oleate (■), oleic acid (●) and triolein (▲). Reactions conditions: $T=260^{\circ}\text{C}$, $p=60\text{ bar}$, $\text{GOR}=10,320\text{ Ni kg}^{-1}\text{ h}^{-1}$ with 2000 ppm H_2S in the feed.

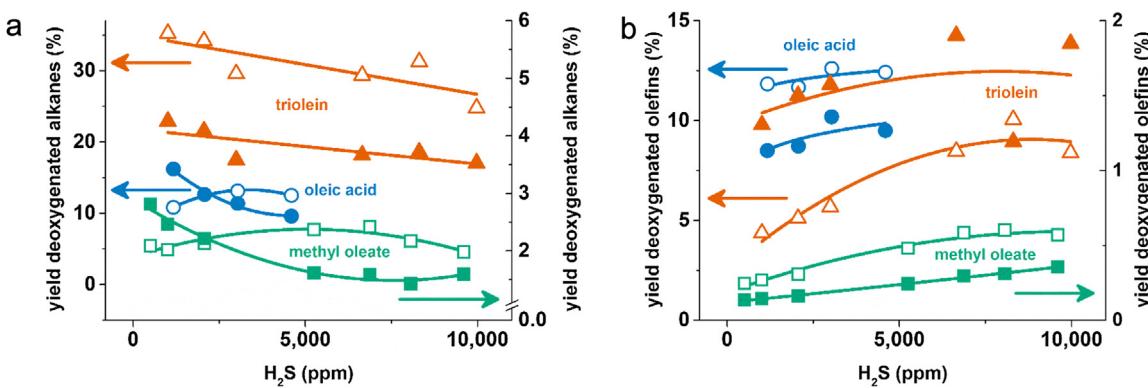


Fig. 5. Yield of (a) *n*-alkanes and (b) olefins with respect to concentration of co-fed H_2S , when using either methyl oleate (■), oleic acid (●), or triolein (▲) as a feedstock. Open and closed symbols represent C17 and C18 carbon chain length respectively. The lines are meant to guide the eyes. Reactions were performed at $T=260^{\circ}\text{C}$, $p=60\text{ bar}$, $\text{GOR}=10,320\text{ Ni kg}^{-1}\text{ h}^{-1}$ with 2000 ppm H_2S in the feed.

and fatty alcoholic intermediates. During oleic acid HDO, the oleic acid concentration is much higher than during methyl oleate HDO. Consequently, the rate of esterification of alcohol intermediates with oleic acid is much higher during oleic acid HDO. Scavenging of these alcohol intermediates by oleic acid explains the much higher C17 selectivity in oleic acid HDO in comparison with methyl oleate HDO. The influence of H_2S on the HDO of oleic acid was also studied (Figs. 4 and 5). In addition to the negative effect on the hydroge-

ation of oleic acid (Fig. 4a), there was an optimum in the H_2S content of the feed with respect to C17 selectivity (Fig. 5a). This optimum can be explained by the competition between competitive adsorption (hindering hydrogenation reactions) and a promoting effect of H_2S on decarbonation, which was noted before in our methyl oleate HDO experiments.

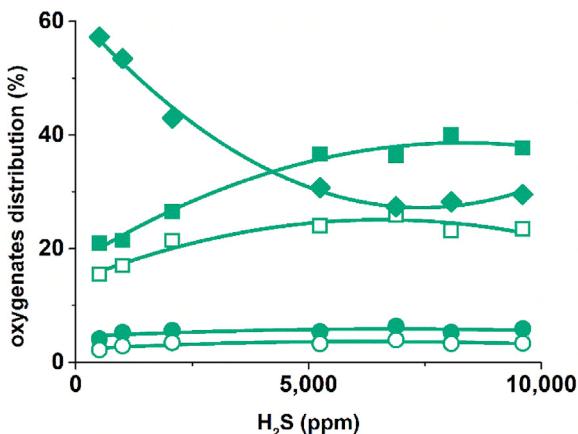


Fig. 6. Distribution of methyl stearate (♦), methyl oleate (■) and oleic acid (●) in the product stream with respect to concentration of H₂S during HDO of methyl oleate. Open and closed symbols represent *cis*- and *trans*-isomers respectively. Reaction conditions: T = 260 °C, p = 60 bar, GOR = 10,320 Nl kg⁻¹ h⁻¹.

3.3. HDO reaction network

We briefly discuss the above results in the context of the reaction network in Fig. 1. The significantly higher HDO activity observed with oleic acid as reactant as compared with methyl oleate shows that the hydrolysis step of methyl oleate is controlling the overall

rate to some degree. Direct hydrogenation of the fatty acid to the fatty alcohol is considered to be a relatively slow reaction [27]. Donnici et al. concluded on the basis of model compound studies that the aldehyde intermediate cannot undergo direct hydrogenation but, instead, reacts via keto-enol isomerization [6]. Alcohols can then be rapidly deoxygenated to olefins and paraffins. Our results show that competitive adsorption of the reactant inhibits the direct HDO route to C18 hydrocarbons more substantially than the decarbonation route to C17 hydrocarbons. The influence of water by-product of the HDO reaction on the selectivity is relatively small.

Next to the removal of oxygen, saturation of double bonds takes place. No doubly unsaturated products were observed despite their minor presence in the feedstock. The absence of unsaturated analogs of stearyl stearate indicates that octadecanol was the only alcoholic reaction intermediate. This result shows that the hydrocarbon chain is already fully saturated before the second oxygen is removed from the intermediates. It is in keeping with the ease of hydrogenation, as double bonds can already be saturated at low temperatures (100–180 °C) over hydrotreating catalysts, i.e., at temperatures too low for deoxygenation to take place [26]. Careful analysis of the C17 and C18 olefins showed that these olefins include predominantly 1-olefins with some products of isomerization towards more stable internal alkenes. This result suggests that the olefins are predominantly formed via decarbonylation of the aldehyde and deoxygenation of alcohols, respectively.

Double bond isomerization is in competition with their hydrogenation. Fig. S3 (see Supplementary information) shows the extent

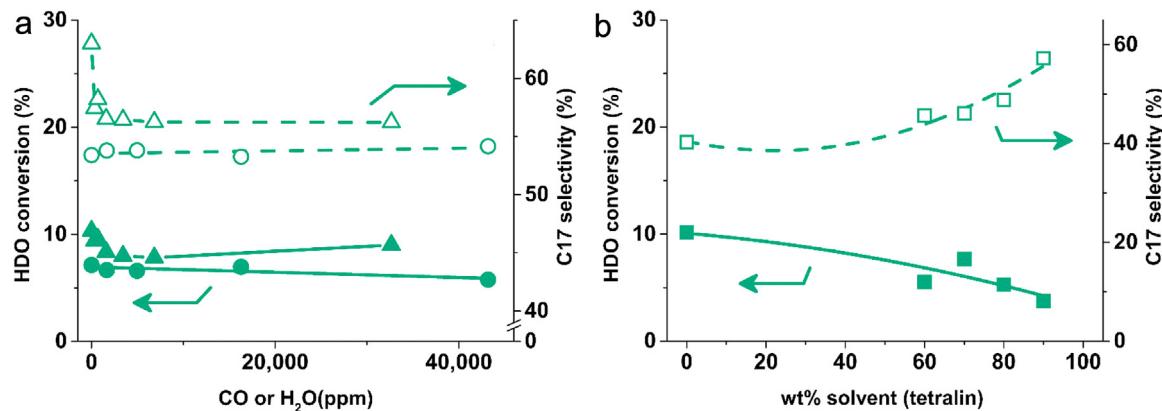


Fig. 7. HDO conversion and C17 selectivity during methyl oleate HDO with respect to concentration of (a) co-fed CO (●) and H₂O (▲) and (b) solvent (tetralin, ■). Reaction conditions: T = 260 °C, p = 60 bar, GOR = 10,320 Nl kg⁻¹ h⁻¹ with 2000 ppm H₂S in the feed.

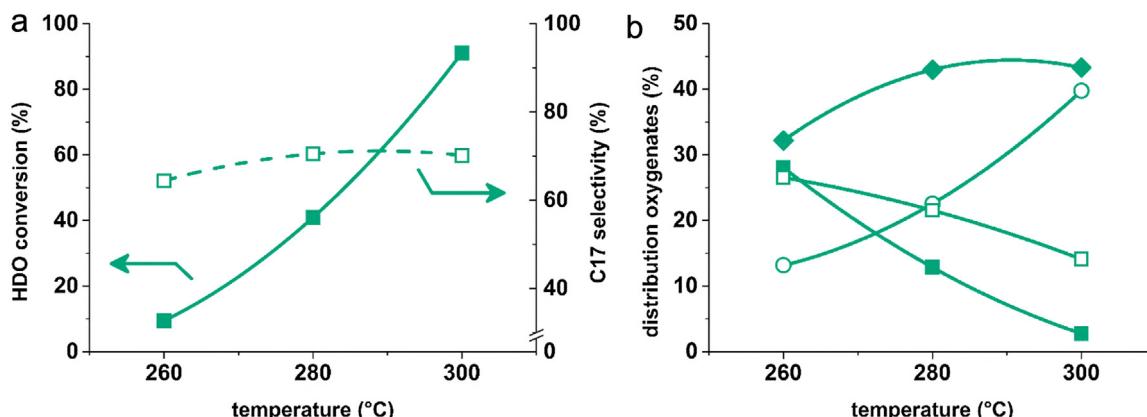


Fig. 8. (a) HDO conversion and C17 selectivity and (b) distribution of methyl stearate (♦), methyl oleate (■), and oleic acid (●) during methyl oleate HDO at different temperatures. Open and closed symbols represent *cis*- and *trans*-isomers respectively. Reaction conditions: T = 260 °C, p = 60 bar, GOR = 10,320 Nl kg⁻¹ h⁻¹ with 2000 ppm H₂S in the feed.

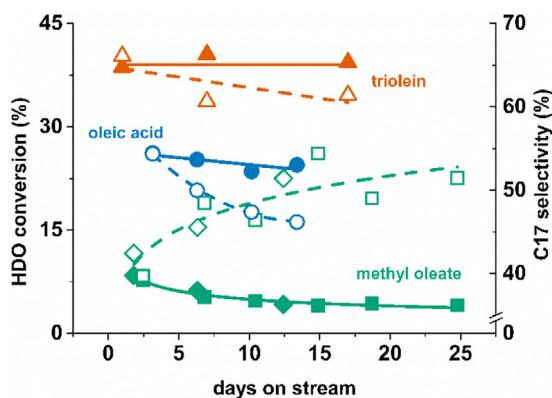


Fig. 9. HDO conversion of oxygenates (closed symbols, left axis) and C17 selectivity (open symbols, right axis) over time using methyl oleate (■, ▲, representing different runs, both with fresh catalysts), oleic acid (●) and triolein (▲) as feedstocks. Reaction conditions: $T = 260^\circ\text{C}$, $p = 60$ bar, $\text{GOR} = 10,320 \text{ NL kg}^{-1} \text{ h}^{-1}$ with 2000 ppm H_2S in the feed.

of isomerization towards internal alkenes vs. the olefin selectivity. The datasets show opposite trends for these two competing reactions. This apparent contradiction can be understood by considering the nature of the experiments. The decreased olefins selectivity, which is evident from Fig. S3a, is due to the lowering of the feedstock concentration (i.e., increasing the residence time and consequently increasing conversion), which increases the rate of double bond hydrogenation. On the other hand, the decreased olefins selectivity (Fig. S3b) correlates with increased H_2S concentration. In conclusion, both datasets emphasize the influence of competitive adsorption on the extent of the double bond isomerization.

Next to this, we also observed that the double bond of the feedstock and oxygen-containing intermediates was not isomerized. This indicates that isomerization of long-chain olefins is slow, which is in accordance with the finding that co-feeding 1-octadecene during methyl oleate HDO did not affect the position of the double bond in the C18 olefins. 1-Octadecene was fully hydrogenated under standard conditions, which shows that only terminal olefin intermediates already adsorbed to the catalyst surface undergo double bond shift. Whereas the catalytic activity and more specifically the hydrogenation activity was seen to decrease over time, the double bond isomerization did not decrease over time. This implies that isomerization takes place on different sites. The involvement of the alumina support might explain the nearly unaffected isomerization activity as compared to the continuous loss of the hydrogenation activity during methyl oleate HDO. This aspect was investigated by using a bare γ -alumina support (Ketjen CK-300, pore volume 0.66 ml/g, surface area 263 m²/g) as the catalyst. The support was not able to isomerize 1-octadecene under standard reaction conditions. An additional experiment with an activated carbon supported NiMoS catalyst (6.7 wt% Mo, 1.3 wt% Ni, co-impregnated with nitrilotriacetic acid [48], supported on carbon Norit RX-3 Extra, pore volume 1.0 ml/g, surface area 1190 m²/g) led to formation of isomerization products similar to the alumina-supported catalyst. The result of these experiments show that acid sites of the support are not involved in isomerization reactions. Indirectly, the similar product distributions of the isomerization of both major deoxygenation pathways confirm the small contribution of direct hydrogenolysis of the intermediate alcohol [22], i.e., both deoxygenation routes proceed via formation of 1-olefins.

3.4. Catalyst deactivation

Fig. 9 shows that the HDO conversion of methyl oleate slowly decreased with time on stream for the sulfided NiMo catalyst under

standard reaction conditions. The reaction time investigated here is much longer than the 6 h on stream evaluated by Coronado and co-workers [32,33]. With decreasing conversion, the selectivity towards C17 products increased at the expense of C18 products. The relative rate of the double bond hydrogenation of methyl oleate to methyl stearate also decreased, as can be seen in Fig. 10. The selectivity towards olefins increased over time. These three observations point to the decrease of the hydrogenation activity of the catalyst with time on stream. Decarbonation was less affected by deactivation. These observations suggest that direct HDO and decarbonation reactions take place on different sites. This aspect has also been mentioned in work of the Krause group [25]. Work done by Ruinart de Brimont et al. showed that MoS_2 was more selective towards direct HDO, while the contribution of decarbonation was increased by using promoters [49].

The conversion during oleic acid also HDO decreased with time on stream but to a lesser extent than during methyl oleate HDO (Fig. 9). We observed that the C17 selectivity decreased with time on stream during oleic acid HDO, which contrasts the observations made for methyl oleate HDO. We speculate that this is due to the deactivation of the catalyst functionality involved in the esterification of oleic acid with intermediate alcohols. This is also in keeping with the decrease of the stearyl stearate amount with time on stream. The apparent contradiction concerning the C17 selectivity between the two reactants can be understood by taking into account the formation of stearyl stearate, which is the product of the reaction of the intermediate alcohol with hydrogenated oleic acid [26]. Whereas acids can yield both C17 and C18 products, the subsequent intermediate alcohol will only undergo removal of water and lead to C18 hydrocarbons. The rapid formation of stearyl stearate with oleic acid as reactant explains the lower C17 selectivity as compared with methyl oleate HDO. As these fatty acid esters are secondary products, longer contact times will favor their conversion to hydrocarbons. By nature, longer alkyl esters are less stable than methyl esters [50]. Over time, the overall activity decreases, leaving more intermediate stearyl stearate (Supplementary information S4). This results in decreased C17 selectivity.

Structural changes and oxidation of the catalyst are possible causes for catalyst deactivation [22,25]. To distinguish these, we characterized spent catalysts in detail. XPS was used to establish whether impurities in the feedstock deactivated the catalyst. During production of alkyl esters, impurities such as Na, Mg, P, K, Cl, Ca, Cr, Zn or Sn may end up in the final product [36]. Alkali metals can lower the performance of hydrotreating catalysts in HDS [51] and HDO [28] reactions. However, XPS showed that such poisons were not present in significant amounts on the spent catalyst (i.e., after one week methyl oleate HDO). We explicitly focused on the presence of Cl, as this may cause corrosion to steel reactors. As a precaution, we used Hastelloy reactors in all our HDO experiments. XPS spectra of the (sulfided) reference and spent catalysts are shown in Fig. 11. The Mo 3d spectrum is mainly composed of MoS_2 and a small contribution of Mo-oxysulfides and – oxides. The Mo 3d spectra were fitted with three doublets, representing Mo^{4+} , Mo^{5+} , and Mo^{6+} [52]. This region of the spectrum also contains the S 2s peak. The Ni 2p_{3/2} spectra contain contributions of Ni in NiS and NiO environments. Shake-up features related to these species are also seen at higher binding energy [53]. The Mo 3d and Ni 2p binding energies of the reference sulfided catalyst as well as representative spectra with fitting results can be found in the Supplementary information (Fig. S5 and Table S6). Quantitative results are given in Table 1.

Qualitatively, the Ni and Mo spectra did not show significant changes as a function of the reaction time. The fit results evidence that the sulfidation degree of Ni and Mo did not change appreciably during the methyl oleate HDO reaction. The sulfidation degree of Mo is around $90\% \pm 2\%$ and that of Ni around $85\% \pm 2\%$. Isotopic

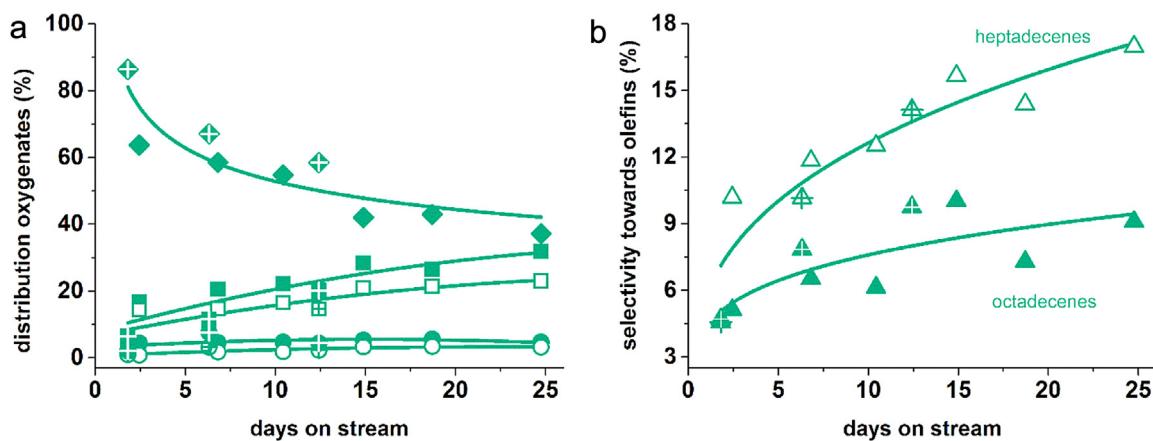


Fig. 10. (a) Distribution of methyl stearate (♦), methyl oleate (●), and oleic acid (■) in the product mixture. Open and closed symbols represent *cis*- and *trans*-isomers respectively. Crosses refer to different reaction experiments with fresh catalyst to show effect of catalyst deactivation; (b) Distribution of olefins (▲) over time. Open and closed symbols represent heptadecenes and octadecenes, respectively. Reaction conditions: $T = 260^\circ\text{C}$, $p = 60$ bar, $\text{GOR} = 10,320 \text{ NI kg}^{-1} \text{ h}^{-1}$ with 2000 ppm H_2S in the feed.

Table 1

Characterization of fresh and spent catalysts and reference samples by XPS, TEM and N_2 physisorption.

Sample	Atomic ratios from fitting XPS spectra ^a							TEM		BET ^e	
	$\text{Mo}_{\text{total}}/\text{Al}$	$\text{Mo}^{4+}(\%)^b$	$\text{Mo}^{5+}(\%)$	$\text{Mo}^{6+}(\%)$	Ni/Al	$\text{NiS}/\text{Ni}_{\text{total}}$	Ni/Mo	C/Al	slab length ^c (nm)	stacking ^d (–)	surface area (m^2/g)
Alumina	–	–	–	–	–	–	–	–	–	–	183
Fresh catalyst	–	–	–	–	–	–	–	–	–	–	185
Spent, 0 h ^f	0.066	88	9	4	0.016	0.83	0.24	0.77	3.30	1.9	160
Spent, 1 h	0.055	91	5	4	0.014	0.86	0.26	1.2	3.26	1.6	–
Spent, 24 h	0.048	88	8	4	0.013	0.83	0.27	1.2	3.47	2.1	–
Spent, 1 week	0.062	91	5	4	0.016	0.88	0.25	2.2	3.32	2.2	138
Spent, 1 week ^g	0.065	92	5	4	0.018	0.84	0.28	3.3	3.16	1.8	–

^a Based on relative sensitivity factors based on Scofield cross-sections.

^b Sulfidation degree.

^c Determined by fitting a log-normal distribution, 95% confidence norm is 0.1 nm.

^d 95% confidence norm is 0.1 (–).

^e Isotherms shown in Fig. S11 (see Supplementary information).

^f Sulfidized in reactor, no exposure to reaction mixture.

^g Co-feeding 10,000 ppm H_2S instead of 2000 ppm H_2S .

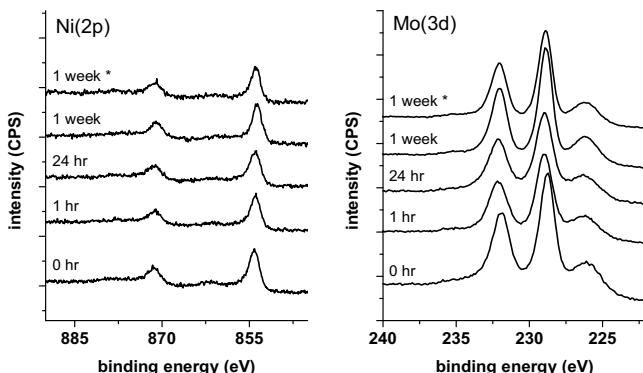


Fig. 11. XPS spectra of $\text{NiMoS}/\text{Al}_2\text{O}_3$ before and after HDO of methyl oleate with (left) the $\text{Ni}(2\text{p})$ and (right) the $\text{Mo}(3\text{d})$ and $\text{S}(2\text{s})$ regions. The spectra have been normalized to the $\text{Al}(2\text{p})$ of the support. Fitting results are provided in Table 1, fitted spectra in the Supplementary information (Fig. S5 and Table S6). Reactions were performed at $T = 260^\circ\text{C}$, $p = 50$ bar, $\text{GOR} = 4750 \text{ NI kg}^{-1} \text{ h}^{-1}$, $\text{WHSV} = 6.5 \text{ h}^{-1}$ with 2000 ppm H_2S in the feed (the sample indicated by an asterisk was obtained by co-feeding 10,000 ppm H_2S).

experiments involving pulses of labelled oleic acid have shown that the sulfur content of the catalyst slightly decreased [31]. We expect that the presence of H_2S in the feed will rapidly remove the oxygen species from the surface. It is also seen that the Mo/Al and Ni/Al ratios do not significantly vary among these samples, which indi-

cates that the dispersion of the two active metals does not change appreciably.

A notable difference between the samples is the increased contribution of carbon (as judged from the XPS C/Al ratio). From the larger amount of carbon in the spent catalysts compared with the adventitious carbon level in the freshly sulfidized catalyst, we infer that carbon species were deposited on the catalyst during the HDO reaction. This is in line with previous work, in which significant increases of carbon (up to 7.5 wt%) were reported [22]. Coke deposition has been mentioned before as a possible reason for the deactivation of metal sulfide based catalysts used in HDO reactions [25].

TEM is the preferred technique to determine the dispersion and morphology of the MoS_2 phase [15]. Representative transmission electron micrographs of a sulfidized and a spent catalyst after 1 week on stream are shown in Fig. 12. The images show the MoS_2 slabs by their edge planes oriented in line with or slightly tilted from the electron beam. The slabs are present as single slabs as well as in the form of stacks. Fig. 12 also shows the slab size distribution for these two samples. The size distributions for the other spent catalysts are collected in the Supplementary information (Fig. S7). The corresponding morphological parameters of the MoS_2 phase derived from the TEM measurements are summarized in Table 1. Clearly, there is no significant change in the average size of the MoS_2 slabs. This shows that the active phase did not sinter during the methyl oleate HDO reaction. Oxidation of the active phase would lead to blurring of the edges of the MoS_2 slabs [39], which

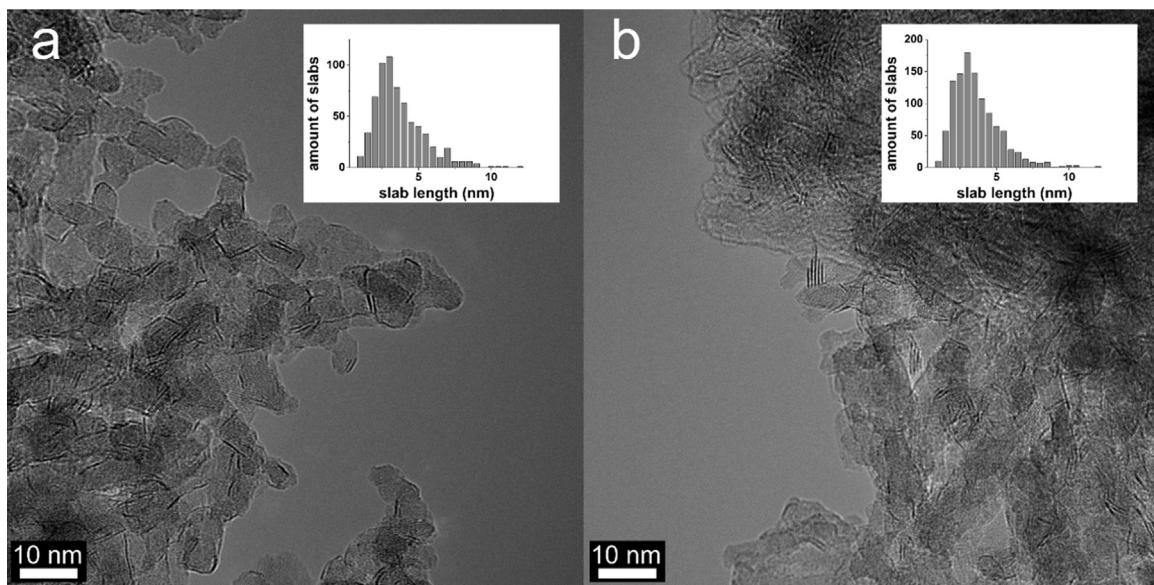


Fig. 12. Representative micrographs of (a) freshly sulfided NiMoS/Al₂O₃ and (b) NiMoS/Al₂O₃ after one week methyl oleate HDO ($T = 260^\circ\text{C}$, $p = 50$ bar, GOR = 4750 Nl kg⁻¹ h⁻¹, WHSV = 6.5 h⁻¹, 2000 ppm H₂S). The inserts show the corresponding slab length distribution.

is not observed in the present set. On the other hand, the stacking degree increased slightly with time on stream. This result may point to a small change in the metal-support interaction, which can for instance be due to the presence of water, which affects the hydroxylation degree of the alumina support. The mobility of the MoS₂ phase has earlier been emphasized by Eijsbouts [17]. On the other hand, it is usually reported that increased stacking due to high-temperature sulfidation goes together with lateral growth of slabs [54]. The increase in stacking may influence the catalytic performance. For instance, Daage and Chianelli [55] and Hensen and co-workers [56] have argued that stacking affects the hydrogenation activity of these catalysts. Based on STM observations, it has also been shown that rim sites of MoS₂ slabs contain metallic states [57], which are presumably involved in hydrogenation reactions [55,56]. Stacking of the MoS₂ slabs would thus decrease the number of such exposed rim sites and in this way lower the hydrogenation activity.

We also established that formation of boehmite did not occur under the given reaction conditions. In hot liquid water as employed during aqueous phase reforming of biomass model compounds [58], it has been found that γ -alumina will be slowly transformed into boehmite. Comparing the ²⁷Al MAS NMR and XRD data for reference and spent catalysts (Figs. S8–S10 in the Supplementary information) did not show significant changes in the nature of the alumina support, from which we could exclude that phase transformation of the support occurs during methyl oleate HDO.

So far, the characterization data point to carbon deposition and increased stacking as dominant changes during the HDO of methyl oleate. We further investigated the surface of the spent catalysts to understand the nature of the carbon deposition. After one week of reaction, about 14% of the BET surface area was lost (Table 1) and the average pore diameter decreased (Supplementary information, Fig. S11). TGA weight loss curves, which are shown in Fig. 13, contain two main oxidation features. The first one at low temperature ($\sim 270^\circ\text{C}$) is also seen for the fresh catalyst and can accordingly be assigned to oxidation of sulfide species [59]. The second one, only observed for the spent catalysts, is a much broader feature between 200 °C and 480 °C, indicative of the oxidation of carbonaceous deposits. The total carbon content in the spent cata-

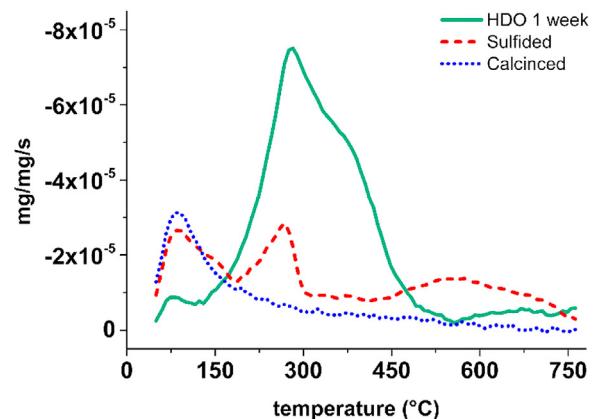


Fig. 13. TGA weight loss curves of spent catalysts and reference materials.

lyst (estimated by subtracting the weight loss due to oxidation of the metal sulfide phase) is about 10 wt%.

Diffuse reflectance infrared FT spectroscopy (DRIFTS) of the sample used in methyl oleate HDO for one week predominantly shows aliphatic stretches and bends (Fig. S12 in the Supplementary information). The spectrum does not contain aromatic C–H stretches, which excludes the presence of tetralin-derived species at the catalyst surface. The main features are aliphatic stretch vibrations at 2850 cm⁻¹ and 2990 cm⁻¹ [60]. The spectrum also contains a shoulder in the 1700 cm⁻¹–1750 cm⁻¹ region due to the C=O stretch in esters. Both 1550 cm⁻¹ and 1450 cm⁻¹ bands are assigned to carboxylate. The band at 1450 cm⁻¹ can also be due to methyl and methylene bending modes. The 950 cm⁻¹ is assigned to the C–H out-of-plane bend next to a double carbon–carbon bond. All of this suggests that some of the reactant molecules have deposited on the catalyst surface, presumably in oligomerized form. Some of the frequencies observed (i.e., 950 cm⁻¹ and 1450 cm⁻¹) might be assigned to aromatic ring (aryl) bends and stretches. However, as many of the other characteristic aromatic group frequencies (mainly between 670 and 900 cm⁻¹) are absent, we discard their presence. The absence of tetralin adsorbing in large amounts to the catalyst is also in line with the Raman spectrum of the spent sample (Fig. S13 in the Supplementary information).

3.5. HDO of triolein

Methyl oleate and oleic acid were chosen as model compounds with the aim to gain insight into the reaction network of the HDO of fatty acid methyl esters and fatty acids. We compare these data to HDO experiments with triolein (glyceryl trioleate) as the most representative model compound for vegetable oil feedstock. It was observed that triolein was nearly completely converted in single chain products with only approximately 3% remaining in the form of mono- and di-glycerides. This is consistent with the notion that triglycerides are more easily hydrolysed than methyl esters [2,41]. Only below 200 °C, unconverted triglyceride was observed. The data were insufficient to draw conclusions on any specificity with regard to the removal of the fatty acids. The amounts of acid intermediates were more than ten times larger during triolein HDO (normalized per feedstock molecule) compared with methyl oleate HDO. The overall HDO activity and the C17 selectivity are shown in Fig. 2. As the conversion of the reactant was complete, we could not determine the reaction order with respect to triolein. The selectivity trends for triolein HDO were very similar to those observed for oleic acid. This is consistent with the observation that acids were rapidly formed by the cleavage of the bonds between the acid and the glyceryl unit. Fig. S14 (see the Supporting information) shows the yield of C17 and C18 hydrocarbons as a function of reactant conversion for methyl oleate, oleic acid and triolein HDO. These plots emphasize the different dependence of direct HDO and decarbonation routes on HDO conversion. The similarity of the plots for methyl oleate and oleic acid suggest that competitive adsorption of intermediate acids explains the dependence of the selectivity (direct HDO vs. decarbonation) on HDO conversion. This is in keeping with the higher C17 yield during triolein HDO, as in these experiments the concentration of acid intermediates is significantly higher. The similar dependence of the yields on conversion suggests that the underlying mechanism by which C17 and C18 hydrocarbons are formed is very similar for the three reactants.

Fig. 4 shows the influence of H₂S on the HDO of triolein. H₂S suppresses the overall HDO activity as also observed for the HDO of the other model compounds. Increasing the H₂S concentration did not affect the product distribution as significantly as seen during methyl oleate and oleic acid HDO (Fig. 5). The main reaction pathways appear to be equally inhibited by H₂S. The product distributions for the HDO of triolein and methyl oleate were very similar, indicating that methyl oleate is a representative model compound for the HDO of triglycerides in this respect. Slow catalyst deactivation as observed during the HDO of methyl oleate was nearly absent during the HDO of triolein. These observations imply that H₂S plays a role in the hydrolysis of the ester bond in methyl oleate, but not in hydrolysis of triglycerides.

4. Conclusions

HDO of methyl oleate, oleic acid and glyceryl trioleate, used as model compounds for triglycerides, was investigated using a sulfided alumina-supported NiMo catalyst in a single-pass microflow reactor operated at trickle-flow conditions. Reaction temperature and pressure and the concentration of the reactant, CO, H₂S, H₂O and tetralin solvent were varied. The main reaction products were C17 and C18 paraffins and a small fraction of the corresponding olefins. The HDO reactions were first order in the reactant at the conditions studied. Most of the unsaturated bonds in alkyl chains of the feedstock were rapidly hydrogenated. The reaction proceeds via fatty acid intermediates, which are formed by slow hydrolysis of methyl oleate. These intermediates can be either decarbonylated/decarboxylated to C17 hydrocarbons (decarbonation) or hydrogenated to an alcohol intermediate which is then

hydrodeoxygenated to C18 hydrocarbons (direct HDO). The most salient findings of the present study are:

- NiMoS/γ-Al₂O₃ contains sites for (i) hydrolysis of methyl esters, (ii) direct HDO/hydrogenation and (iii) decarbonation. Hydrolysis takes mainly place on the Lewis acid sites of the alumina support. Direct HDO takes place on the active metal sulfide phase and is strongly inhibited by adsorption of the fatty acid intermediates as well as H₂S. Decarbonation, most likely involving decarbonylation, takes place on a different site and is promoted by H₂S.
- H₂S, H₂O, CO and the tetralin solvent only very slightly inhibit the overall HDO activity.
- NiMoS/Al₂O₃ slowly deactivated during methyl oleate HDO under standard conditions (T = 260 °C, p = 60 bar, GOR = 10,320 Nl kg⁻¹ h⁻¹, 2000 ppm H₂S). During deactivation, the direct HDO/hydrogenation route was affected more substantially than the decarbonation route. In the presence of H₂S, no oxidation of the active metal sulfide phase was observed. Slightly increased stacking of the active phase after one week on stream, presumably due to water, may be at the origin of the decreased hydrogenation activity, while heavy products on the catalyst surface block Lewis acidic sites involved in the hydrolysis of methyl oleate. The catalyst did not deactivate during glyceryl trioleate HDO, likely because hydrolysis of the glyceride ester bonds does not require a catalyst. The kinetics and mechanism of glyceryl trioleate HDO resemble those of methyl oleate HDO. The value of methyl oleate as a model compound for triglyceride HDO is hampered by the low rate of hydrolysis of the methyl ester compared with hydrolysis of triglycerides.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.08.036>.

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